

# Tuning of competing magnetic and superconducting phase volumes in $\text{LaFeAsO}_{0.945}\text{F}_{0.055}$ by hydrostatic pressure

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The interplay between magnetism and superconductivity in  $\text{LaFeAsO}_{0.945}\text{F}_{0.055}$  was studied as a function of hydrostatic pressure up to  $p \simeq 2.4$  GPa by means of muon-spin rotation ( $\mu\text{SR}$ ) and magnetization measurements. The application of pressure leads to a substantial decrease of the magnetic ordering temperature  $T_N$  and a reduction of the magnetic phase volume and, at the same time, to a strong increase of the superconducting transition temperature  $T_c$  and the diamagnetic susceptibility. From the volume sensitive  $\mu\text{SR}$  measurements it can be concluded that the superconducting and the magnetic areas which coexist in the same sample are inclined towards spatial separation and compete for phase volume as a function of pressure.

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The interplay between superconductivity and magnetism in high-temperature superconductors (HTS) remains an important open issue. In cuprate and Fe-based HTS the superconductivity can be induced in a magnetic parent compound by charge doping and/or by pressure (chemical or external). In most cuprate HTS the transformation from the magnetic into the superconducting state follows an almost common scenario. On increasing the doping level the antiferromagnetically ordered phase develops into a purely superconducting state through a region where a spin-glass type of magnetism coexists with superconductivity [1–3]. The situation with Fe-based HTS is, somehow, different. For some families of Fe-based HTS like e.g.  $\text{SmFeAsO}_{1-x}\text{F}_x$ ,  $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}$ , and  $\text{FeSe}_{1-x}\text{Te}_x$ , the magnetism is continuously suppressed and superconductivity enhanced by changing the F, Co, or Se content. In the intermediate region, bulk magnetism and bulk superconductivity are coexisting in space [4–7]. In  $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$  the magnetic and the superconducting areas are found to be separated microscopically as revealed, e.g., by atomic force microscopy experiments [8].

One of the most interesting cases is realized in the  $\text{LaFeAsO}_{1-x}\text{F}_x$  family of Fe-based HTS demonstrating an *abrupt* (first order like) transition between the magnetic and the superconducting phases. Muon-spin rotation ( $\mu\text{SR}$ ) and Mössbauer experiments show that above a certain  $x$  the samples become purely superconducting without visible traces of magnetism [9]. Such a behavior seems to be rather different from the one observed for the other structurally related families of Fe-based HTS in which the La atom is replaced by Sm, Pr, Ce, etc. All of them demonstrate a coexistence between superconductivity and magnetism for a certain doping level [4, 5, 10]. Consequently the question if a similar coexistence is present in  $\text{LaFeAsO}_{1-x}\text{F}_x$  but within a much

narrower, up to now not detected, doping region or if an abrupt change between the superconductivity and magnetism is a unique property of this particular family of Fe-based HTS needs to be resolved.

Hydrostatic pressure experiments on  $\text{LaFeAsO}_{0.945}\text{F}_{0.055}$ , which is at the border to the superconducting state but still magnetic, were performed to distinguish between two above mentioned possibilities. This approach allows to follow the transformation of the material from the magnetic to the superconducting state in detail on one sample, i.e. without the necessity to synthesize a large number of samples with exactly defined stoichiometry near the phase boundary. Our measurements show that both the magnetic and superconducting states are most probably spatially separated in the crossover region of the phase diagram and compete for phase volume.

The sample with the nominal composition  $\text{LaFeAsO}_{0.945}\text{F}_{0.055}$  was prepared in cubic anvil high-pressure cell from the stoichiometric mixture of LaAs, FeAs,  $\text{Fe}_2\text{O}_3$ , Fe and  $\text{LaF}_3$  [11]. A pressure of  $\simeq 3$  GPa was applied at room temperature. By keeping the pressure constant, the temperature was first ramped up to the maximum value of  $1320^\circ\text{C}$ , kept constant for 5.5 h and then quenched to room temperature within a few minutes.

The superconducting properties of  $\text{LaFeAsO}_{0.945}\text{F}_{0.055}$  were studied by magnetization experiments. The zero-field-cooled and field-cooled (FC and ZFC) DC magnetization measurements up to  $p \simeq 1.1$  GPa were performed by using the commercial SQUID magnetometer (MPMS-XL7) and a piston-cylinder CuBe pressure cell (“EasyLab Mcell 10“, [12]). The AC experiments up to  $p \simeq 2$  GPa were performed by using a home-made AC magnetometer (AC frequency  $\nu = 72$  Hz, AC field amplitude  $\mu_0 H_{AC} \simeq 0.1$  mT). The two pick-up and the

excitation coils were wound directly around the pressure cell made from MP35N alloy. The sample and the small piece of In, used as the pressure indicator, were located inside the different pick-up coils. Note that the AC experiments within the present geometry (the coils wound outside the pressure cell) require separate measurements of the background signal from the empty cell. For this particular sample, due to the very small superconducting response at ambient pressure (see the discussion below), the AC magnetization data measured at  $p = 0.0$  GPa were used as the background signal.

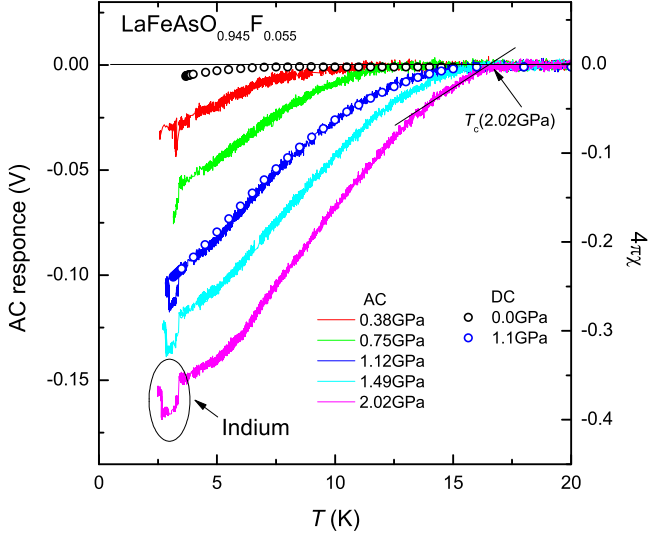


FIG. 1: (color online) AC (solid curves) and ZFC  $\mu_0 H = 5$  mT DC (open symbols) susceptibility curves as a function of temperature for different pressures of  $\text{LaFeAsO}_{0.945}\text{F}_{0.055}$ . The transition temperature  $T_c$  is determined by the intersect of the linearly extrapolated magnetization curve with the zero line. The superconducting transition of pure indium used as a pressure indicator in the AC magnetization experiment is highlighted by the oval for the highest pressure.

The results of the magnetization studies are presented in Fig. 1. At ambient pressure the diamagnetic susceptibility at  $T \simeq 3.5$  K [ $\chi(3.5 \text{ K})$ ] reaches approximately 1% of its ideal value ( $\chi_{\text{id}} = -1/4\pi$ ). This suggests that the superconductivity at  $p = 0.0$  is just filamentary and it is present only within a small volume of the sample. With increasing pressure both, the onset temperature of the superconducting transition  $T_c$  [determined from the intersect of the linearly extrapolated  $\chi(T)$  in the vicinity of  $T_c$  with the zero line, see Fig. 1] and the low-temperature value of the diamagnetic response ( $-4\pi\chi$ ), increase quite substantially. According to Fig. 1, the increase of the external pressure from  $p = 0.0$  to 2.02 GPa leads to the shift of  $T_c$  from  $\simeq 7$  to  $\simeq 16$  K and to an increase of  $-4\pi\chi$  from  $\sim 1$  to  $\sim 35\%$ . An additional set of DC magnetization measurements at  $p \simeq 1.1$  GPa show that the diamagnetic response reduces by a factor 2 for an applied field of 1 mT in ZFC and to a value of  $4\pi\chi \simeq -0.05$  in  $\mu_0 H = 5$  mT FC experiments, respectively (both are not shown). Such differences, which could be caused by the

effect of pinning and the presence of weak links between the superconducting areas, do not permit a reliable evaluation of the genuine superconducting volume. One may only conclude that the superconducting volume fraction increases with increasing pressure but is always smaller than the whole sample volume.

The magnetic properties of  $\text{LaFeAsO}_{0.945}\text{F}_{0.055}$  were studied in zero-field (ZF) muon-spin rotation experiments. Pressures up to  $\simeq 2.4$  GPa were generated in a double wall piston-cylinder MP35N cell. Few repre-

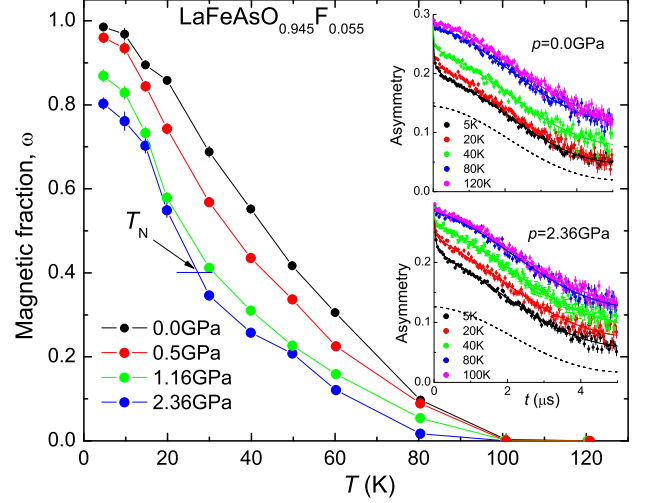


FIG. 2: (color online) Temperature dependence of the magnetic volume fraction of  $\text{LaFeAsO}_{0.945}\text{F}_{0.055}$  at various pressures. The insets show the ZF muon-time spectra at  $p = 0.0$  and 2.36 GPa. The solid lines are fits by means of Eq. (1). The dotted lines represent the response of the pressure cell.

sentative muon-time spectra measured at  $p = 0.0$  and 2.36 GPa are shown in the insets of Fig. 2. The data were analyzed by decomposing the signal on the contribution of the sample and the pressure cell as:

$$A(t) = A_S(0) P_S(t) + A_{PC}(0) P_{PC}(t). \quad (1)$$

Here  $A_S(0)$  and  $A_{PC}(0)$  are the initial asymmetries and  $P_S(t)$  and  $P_{PC}(t)$  are the muon-spin polarizations belonging to the sample and the pressure cell, respectively.  $P_{PC}(t)$  was measured in an independent experiment. The response of the sample was assumed to consist of a magnetic and a nonmagnetic contribution and described as:

$$P_S(t) = \omega \left[ \frac{1}{3} e^{-\Lambda_{m,l}t} + \frac{2}{3} \left\{ \zeta e^{-\Lambda_{m,t1}t} + (1 - \zeta) e^{-\Lambda_{m,t2}t} \right\} \right] + (1 - \omega) e^{-\Lambda_{pm}t}.$$

Here  $\omega$  is the relative weight (volume) of the magnetic fraction.  $\Lambda_{m,l}$ ,  $\Lambda_{m,t1}$  and  $\Lambda_{m,t2}$  are the exponential depolarization rates representing the longitudinal (1/3) and the transversal (2/3) relaxing components within the parts of the sample being in the magnetic state. Two components within the curly brackets account for contributions of two different muon stopping sites [13] with the relative weight  $\zeta$  and  $(1 - \zeta)$ , respectively.  $\Lambda_{pm}$  is

the relaxation within the parts of the sample remaining nonmagnetic. The exponential character of this relaxation instead of normally expected Kubo-Toyabe kind of behavior [14] is probably caused by the presence of the small amount of magnetic impurities, similar to the one observed in the so called '11' family of Fe-based HTS (see e.g., Refs. 7, 15). For each particular pressure the whole set of the data was fitted simultaneously with  $A_S(0)$ ,  $A_{PC}(0)$ ,  $\zeta$  and the ratio  $\Lambda_{m,t1}/\Lambda_{m,t2}$  as common and  $\omega$ ,  $\Lambda_{m,l}$ ,  $\Lambda_{m,t1}$  and  $\Lambda_{pm}$  as individual parameters for each temperature point. The solid lines in the insets of Fig. 2 represent the result of the fit. The contribution from the cell at  $T = 5$  K is shown as a dotted line.

The main panel of Fig. 2 shows the dependence of the magnetic fraction  $\omega$  on temperature for  $p = 0.0, 0.5, 1.16$ , and  $2.36$  GPa. Two important points need to be considered. First of all, the magnetic volume fraction at each particular temperature is lowered by the application of pressure. Most noteworthy, with increasing pressure an increasingly large part of the sample remains in the paramagnetic state down to lowest temperatures. Second, the magnetic ordering temperature  $T_N$ , defined as the temperature where the magnetic fraction reaches 50% of its maximum low-temperature value, initially decreases with increasing pressure but then demonstrates a tendency to saturate.  $\omega(T)$  curves at  $p = 1.16, 1.92$  (not shown) and  $2.36$  GPa being normalized to their values at  $T \simeq 5$  K become almost identical.

In order to compare the influence of the pressure on the superconducting and the magnetic properties of  $\text{LaFeAsO}_{0.945}\text{F}_{0.055}$  the dependences of  $T_N$ ,  $T_c$ ,  $\omega$ , and  $4\pi\chi$  as a function of  $p$  are plotted in Fig. 3. The decrease of  $T_N$  and  $\omega$  is associated with the corresponding increase of  $T_c$  and  $4\pi\chi$ . By applying a pressure of  $2.36$  GPa,  $T_N$  decreases from  $44$  K to  $27$  K, while  $T_c$  more than doubles from  $\simeq 7$  K to  $\simeq 16$  K upon the application of  $2.02$  GPa.

It should be noted here that the above presented data are pointing to a competition of superconductivity and magnetism, but alone do not allow to answer the question on how these two forms of order coexist within the  $\text{LaFeAsO}_{0.945}\text{F}_{0.055}$  sample. There are three possible scenarios. The first one is the so called *phase separation* scenario according to which the superconductivity develops just within the parts of the sample remaining nonmagnetic down to low temperatures. Such a phase separated coexistence was observed, e.g., in  $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$  [8, 16]. The second possibility is an *atomic* coexistence of the superconducting and magnetic order parameters, which is consistent with models proposed in Refs. 17, 18 and most probably realized within the so-called '11' family of Fe-based HTS [7, 19]. The third possibility is a *nanoscale* segregation into magnetic domains, similar to that reported for cuprate HTS [2, 20, 21]. In underdoped cuprate HTS, static, short-range, stripe-like magnetic correlations are thought to exist in the superconducting state and are assumed not to affect the superconducting carriers [2]. Muons are sensitive to dipolar fields at a distance of up to a few lattice spacings, so if nano-

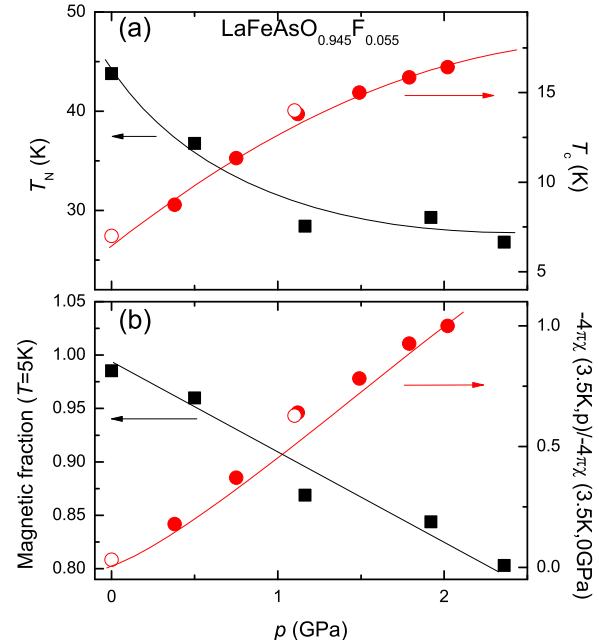


FIG. 3: (color online) (a) Dependence of the magnetic ordering temperature  $T_N$  and the superconducting transition temperature  $T_c$  on pressure. The closed and the open circles correspond to  $T_c$  as obtained in AC and DC magnetization experiments, respectively. (b) The magnetic fraction at  $T = 5$  K and ZFC diamagnetic susceptibility  $-4\pi\chi$  at  $T = 3.5$  K,  $\mu_0 H = 5$  mT as a function of pressure. The closed and the open circles refer to the data obtained in AC and DC magnetization experiments, respectively. The lines are guide for the eye.

scale magnetic domains exist then the fraction of muons experiencing static local magnetic fields could be significantly higher than the fraction of Fe sites carrying an ordered moment. Such type of coexistence was found to be realized within the  $\text{SmFeAsO}_{1-x}\text{F}_x$  and  $\text{CeFeAsO}_{1-x}\text{F}_x$  families of Fe-based HTS [5, 10].

Since the muon is a local probe, the  $\mu\text{SR}$  signals from spatially different areas of the sample are not averaged but superimposed in the measured spectra. This feature allows to distinguish between the three above mentioned scenarios. As discussed above, the ZF- $\mu\text{SR}$  response of the magnetic areas of the sample is characterized by a fast relaxing signal visible at early times of the spectra, while a non-magnetic volume shows slow relaxation, better visible at longer times, only. In Fig. 4, two ZF muon-time spectra taken at the same temperature ( $T = 2.6$  K) and pressure ( $p = 2.36$  GPa) with different magnetic histories are shown. The first muon-time spectra was recorded after cooling the sample from  $T \simeq 100$  K to  $2.6$  K in zero magnetic field. By keeping the temperature constant, the second ZF spectra was obtained after ramping the magnetic field up to  $\mu_0 H \simeq 0.1$  T and then setting it back to zero. Apparently, the ZF- $\mu\text{SR}$  response of the magnetic areas of the sample, as evidenced by the identically fast relaxations  $\Lambda_{m,t1}$  and  $\Lambda_{m,t2}$  at early times of the spectrum (see Fig. 4b and Table I), is not affected by

the magnetic history. On the contrary, the ZF- $\mu$ SR signal representing the non-magnetic volume of the sample exhibits a strongly larger relaxation  $\Lambda_{\text{pm}}$  after the application of an external field at low temperatures (see Fig. 4c and Table I). This indicates that the superconductivity is most probably located within the non-magnetic areas of the sample, since any changes of the magnetic field within a superconductor with non-zero pinning leads to trapping the magnetic flux and, as a consequence, to a very nonuniform field distribution inside the superconducting parts of the sample [22].

Our results point to a strong difference between  $\text{LaFeAsO}_{1-x}\text{F}_x$  and the structurally related families of Fe-based HTS with the La atom substituted by other rare earths elements like Sm, Ce, Pr, Nd etc. In these families bulk magnetism and bulk superconductivity are found to coexist on the nanoscale level [4, 5, 10]. The magnetization and  $\mu$ SR experiments reveal that in  $\text{LaFeAsO}_{1-x}\text{F}_x$ , the magnetism and superconductivity are not coexisting over the whole sample volume, i.e. this system is inclined towards phase separation. The reduction of the magnetic interaction and the simultaneous appearance of superconductivity indicate a much stronger competition of the two ordered parameters.

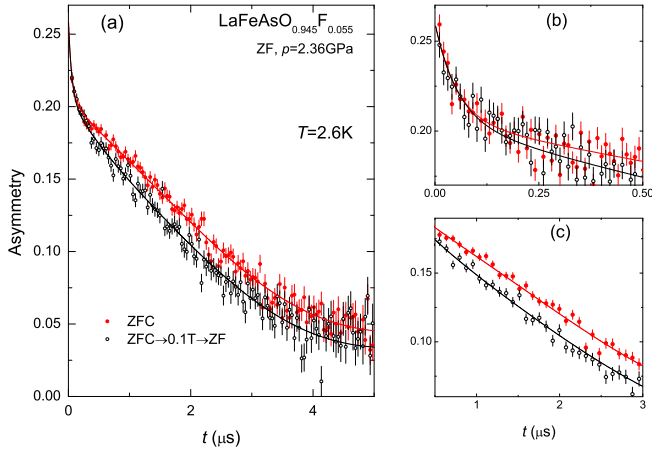


FIG. 4: (color online) (a) The ZF  $\mu$ SR time spectra obtained after cooling the sample in zero magnetic field from  $T \simeq 100$  K down to 2.6 K (red symbols) and after sweeping the magnetic field to 0.1 T and then setting it back to 0.0 without changing the temperature (black symbols). The panels (b) and (c) show the extended parts of the muon-time spectra at the lower and the higher time, respectively. The solid lines are fits by means of Eq. (1).

In conclusion, the interplay between magnetism and superconductivity was studied in  $\text{LaFeAsO}_{0.945}\text{F}_{0.055}$  by performing muon-spin rotation and magnetization experiments as a function of pressure up to  $p \simeq 2.4$  GPa. At ambient pressure the sample is purely magnetic, but at the border to the superconducting state of  $\text{LaFeAsO}_{1-x}\text{F}_x$ . The application of hydrostatic pressure

leads to a substantial decrease of  $T_N$  and reduction of the magnetic phase volume and, at the same time, to a strong increase of  $T_c$  and the diamagnetic susceptibility.

	$\Lambda_{m,t1}$ ( $\mu\text{s}^{-1}$ )	$\Lambda_{m,t2}$ ( $\mu\text{s}^{-1}$ )	$\Lambda_{\text{pm}}$ ( $\mu\text{s}^{-1}$ )
ZFC	19.7(2.7)	1.28(14)	0.165(26)
ZFC→0.1 T→ZF	18.4(3.5)	1.20(28)	1.20(36)

TABLE I: Parameters as extracted from the fit of Eq. (1) to the muon-time spectra obtained after cooling the sample from  $T \simeq 100$  K to 2.6 K in zero magnetic field (ZFC) and after ramping the magnetic field up to  $\mu_0 H \simeq 0.1$  T and setting it back to zero (ZFC→0.1 T→ZF).  $A_S$ ,  $A_{\text{PC}}$ ,  $\zeta$  and  $\omega$  were assumed to be the same for both spectra.

Magnetic history dependent ZF- $\mu$ SR measurements show that superconductivity most probably develops in the areas of the sample that are non-magnetic down to lowest temperatures. This clearly shows that in  $\text{LaFeAsO}_{1-x}\text{F}_x$  magnetism and superconductivity are competing order parameters.

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